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February 13, 1998

Memorandum

To: Susan Svirsky, Tim Prior, Ken Finkelstein
From: Greg Tracey
Subject: ERA Avian Food Chain model.

Dear Raymarkers,

No that I've got all the spreadsheets from Ken I have had a chance to go through Tim's comments and figure out what's going on and what to fix so we can complete the assessment with the new data. Included in the discussion below are some discrepencies that I have discovered, which may explain some of Tim's comments (in italics).

1. The revision seems to have corrected the previous comments related to typographical errors and omissions in the basic food-web model formula 5-1, and the lack of mathematical division using body weights in the use of the formula in Tables 7-14a, b, c and 7-15 (previous General Comment 1 and 2 plus Specific Comments 1a-e and 3).

The values used in Table 7-14a do not agree with those listed in Table 5-1: Intake rates used in for sediment = .006 kg/d ww, but reported as 0.01. Also, intake rate for water used = .050 but reported as 0.054. Since there was no comments on Table 5-1 calculations, I have assumed those are the correct numbers.

a. However, after checking a few of the calculations, it appears that a new math error has cropped up in the calculations for the Red-winged Black Bird, Table 7-15, page 131. It appears that the HR (Home Range) Factor was applied in both the second column, "Insects," and the fifth column, "Total." I believe the HR Factor should have been applied to the "Insects" column and the third column, "Water," or just to the fifth column, but not both as this underestimates the dose.

It looks like the HR factor was only applied to the total. However, the values used in Table 7-15 do not agree with those listed in Table 5-1: Intake rates used in for total food = .0207 kg/d ww, but reported as 0.023 kg/day. The Table heading is also misleading since consumption of insects (0.012, Table 5-1) is only half of the total food estimate. Also, intake rate forBCNH water used = .050 but reported as 0.054. Also, intake rate forRWBB water used = .01 but reported as 0.008. Again, since there was no comments on Table 5-1 calculations, I have assumed those are the correct numbers.

b. The revision now clarifies the bioavailability factor term, BF (Specific Comment 1-e). A bioavailability factor of 65% for copper and 85% for all other contaminants is now used instead of the 100% assumption used in the draft (see page 56, Sect. 5.2 for explanation and Tables 7-14a-c and 7-15 for application).

Confirmed.

2. The revision addresses previous General Comment 3 regarding the apparent 25% under representation of the full daily dietary (prey) requirement of the Black-crowned Night Heron in a slightly different, but acceptable, manner than we had proposed.

a. However, the revision makes this correction by providing an "adjusted HQ" column in Tables 7-14a, b, and c, which is calculated by multiplying the previous, underestimated, Hazard Quotient columns by 1.33 for the missing 25%. This method of adjustment now probably overestimates the dose to some degree by also upwardly adjusting the contribution of the water and, perhaps more significantly, the sediment fractions of the dose. I'd suggest that the 1.33 adjustment factor be applied only to the "prey" or food component of the dose; i.e., fish, crab and insect in the first three columns of Tables 7-14a, b, and c.

This change has been made and is also changed in Table 5-1, with footnote.

b. The 1.33 adjustment seems to be uniformly applied to the BCNH HQ's for all contaminants except copper in Tables 7-14a, b, and c. The copper values seem to be adjusted by a factor of 1.7. I'm not sure why.

This problem is a non-issue when solution 2a is implemented.

3. The revision adds an "allometric scaling" adjustment of the report's literature-derived Reference Toxicity Doses, RTV's (page 124, Sect 7.3.2 and Table 7-13, page 125), which was not in the draft. The adjusted RTV's are then used in Tables 7-14a-c and 7-15 to calculate the HQ's shown in the last two columns of those Tables.

The data used in the spreadsheet for Tables 7-14a-c and 7-15 is the same body wt (kg) as reported in Table 5-1, and would seem needed to get the CoC intake rate into the same units as the RTV benchmark.

I found no further explanation of the method of calculating the scaling factor. Checking several of the values given in Table 7-13 suggests they are calculated with the body-weight based "physiological scaling factor" method described in Equation 4, page 5 of the 1995 revision of the Oakridge National Laboratory's Toxicological Benchmarks for Wildlife, D.M. Opresko et al., June 1995 as follows:

$$NOAEL_{wildlife} = NOAEL_{test} (BW_{test}/BW_{wildlife})^{1/3}$$

However, the more recent revision of the Oakridge National Lab Benchmarks for Wildlife, B.E. Sample, et al., June 1996, changes the power function to 1/4, and, more importantly, no longer recommends using this body size scaling factor for birds based on their review of recent literature. Based on that recommendation, I'd suggest we do the same.

I have revised Table 7-13 to adjust the test RTV only for the extrapolation factor; hence there is no longer a species-specific NOEL, just one for birds.

In any case, the 0.121 kg body weight for the test species (adult hen ring-necked pheasants) for the Dioxin TEQ RTV in Table 7-13, pg. 125, is an error. It should be around 1 kg. Someone skimmed the referenced study, Nosek, et al., and saw figures that are in that report depicting % change in body weights over time that ranged up to approx. 121%. Nosek, et al. (pg. 188) state the initial body weights of the birds was 0.9-1.3 kg.

I have adjusted Table 7-13 to show 1.0 kg for the adult hen ring-necked pheasant body weight.

4. As indicated in the attached copy of our previous comments, we had offered a number of additional, primarily editorial, suggestions. Many of these have been incorporated in the revision. Some were not included.

5. As you indicated that you were going to have additional evaluations made on the TCDD's/TCDF's in Ferry Creek fish, I tried to do some check-calculations to evaluate how these were handled in the revised document. I didn't get far. I can't tell what TEF's were used or how the TEQ's where calculated. I think this difficulty is due to the lack of full data set; i.e., I only seem to be able to find the "total" TCDD'S, PeTCDD'S, HxTCDD'S, etc. in the report, and I haven't found any discussion of TEF's, etc.

I got the TEF table from Steve Stadola at EPA, and used his formulas to calculate the Total Toxicity Equivalency Quotient. All analytes listed in his table were available in the new data set.

6. The Tables containing most of these evaluations in the ERA are in what appears to be handwritten, non-electronic form. This makes it impossible to do any re-writing or recalculation for you. I will fax you copies of three Tables on which I've penciled in some initial thoughts on how they might be edited. These ideas are draft, and may need to be changed as the editing progresses.

Revisions to electronic versions of tables on the included disk are suffixed with "r" after the table name, e.g. Table 7-15 old is "Tab7-15.xls", whereas the revised Table is "Tab7-15r.xls". Note that the new tables are linked together so there aren't any mathematical roll-up errors.

Using the revised input exposure parameter and RTV data in the attached Tables and the site chemistry measured at fish sampling locations; I have drafted a new Table 3.3-1 for the Night Heron exposure scenario for inclusion in the PRG document. As it turned out, two of the fish sampling locations were not evaluated for the TIE (due to non-toxic sediments) hence chemistry data was not collected. There may be data available from the Tetra Tech NUS part of the study. The PCB and dioxin data used was the sum of homolog concentrations and TEQs reported in Table sA-1-1 and A-1-3 of the PRG document.

cc:
M. Penko, USACE
M. Worthy, ENSR

Table 5-1. Avian food web exposure parameters.

SPECIES	INTAKE RATES (kg/day wet weight) [a]						HOME RANGE	BIOAVAILABILITY FACTOR	BODY WEIGHT (kg)
	ORGANISMS			TOTAL FOOD*	INCIDENTAL SEDIMENT	WATER[b] (L/day)			
	FISH	CRUSTACEANS	TERRESTRIAL INSECTS						
Red-winged blackbird	na		0.012	0.023	na	0.008	0.9	COC specific	0.054
Black-crowned night heron[c]	0.177	0.048	0.003	0.172	0.01	0.054	1	COC specific	0.883

(a) Dry to wet weight conversions used mean percent moisture of 78.7% for fish, 68% for crabs, 48% for insects, and 44.5% for sediment.
(b) Values for dietary requirements were derived from allometric equations of Nagy presented in Section 5.
(c) 1.33 adjustment factor be applied only to the "prey" or food component of the dose
to adjust for 25% under representation of the full daily dietary (prey) requirement of the Black-crowned Night Heron

Table 7-13. RTVs for use in the avian food web model and their sources.

Contaminant of Concern	Compound Tested	Test Species: Common name	Body Weight, kg	Condition Evaluated[a]	RTV (mg/kg Bw/day)	Endpoint	Extrapolation Factor[b]	Source	Adjusted NOEL (mg/kg Bw/day)
arsenic	sodium arsenite	mallard	1	M	5.135	Chronic NOEL	1	USFWS 1964	5.14
cadmium	cadmium chloride	mallard	1.153	R	1.45	Chronic NOEL	1	White and Finley 1978	1.45
chromium(3	CrK(SO4)2	black duck	1.25	R	1	Chronic NOEL	1	Hasetine et al., unpub.	1.00
copper	copper oxide	chicken	0.534	G,M	28.13	Chronic NOEL	1	Mehring et al. 1960	28.13
lead	metallic	American kestrel	0.13	R	2.05		1	Paltee 1984	2.05
mercury		mallard	1	R	0.064	LOEL unbounded	0.5	Heinz et al. 1979	0.03
nickel	nickel sulphate	mallard	0.782	M,G	77.4	Chronic NOEL	1	Cain and Pafford 1981	77.40
silver	silver nitrate, chloride, and thiosulfate	chickens	0.4	G	12.5	Subchronic NOEL	1	Hill and Matrone 1970	12.50
zinc	zinc carbonate	chicken	1.9	M	11.3	Chronic NOEL	1	Gasaway and Buss 1972	11.30
Dioxin TEQs	2,3,7,8-TCDD	ringed-neck pheasants	1.0	R	0.000014	Chronic NOEL	1	Noesek et al. 1992	0.000014
Naphthalene	TPH	mallard	1.3	M	338	Chronic LOEL	0.1	Patton and Dieter 1980	33.80
Phenanthrene	TPH	mallard	1.3	M	338	Chronic LOEL	0.1	Patton and Dieter 1980	33.80
DDTS		brown pelican	3.5	R	0.028	Chronic LOEL	0.1	EPA 1993	0.00
PCBs		pheasant	1	R	1.8	Chronic LOEL	0.1	EPA 1993	0.18

a— M: mortality R: reproduction G: growth

b — EPA, 1993: LOEL to NOEL factor of two, rather than ten, was used for Hg because the LOEL appeared to be near the threshold for dietary effects

Table 7-14a. Ingestion rates and doses of CoCs, by media, with Hazard Quotient calculations for the black-crowned night heron.

Ferry Creek

Contaminant of Concern	Dietary Intake, (mg/day)					Total Assimilated (mg/day)	Total Assimilated (mg/kg Bw/day)	RTV (mg/kg Bw/day)	Hazard Quotient
	Fish	Crab	Insects	Sediment	Water				
Arsenic	0.11	0.0766	0.0006	0.0330	0.0012	0.2	0.2	5.14	0.04
Cadmium	0.01	0.0603	0.0025	0.0190	0.0001	0.08	0.09	1.45	0.064
Chromium (+3)	0.28	0.1111	0.0028	0.6600	0.0007	0.9	1.0	1.00	1.02
Copper	1.98	3.4569	0.0745	3.6340	0.0065	5.9	6.7	28.13	0.24
Lead	1.11	0.7565	0.0059	2.5050	0.0007	3.7	4.2	2.05	2.06
Mercury	0.00	0.0005	0.0000	0.0019	0.0000	0.004	0.005	0.0320	0.15
Nickel	0.13	0.1580	0.0024	0.3000	0.0006	0.50	0.6	77.4	0.0074
Silver	0.01	nr	nr	0.0053	0.0001	0.009	0.010	12.50	0.0008
Zinc	8.83	1.3119	0.2062	2.2350	0.0069	10.7	12.1	11.3	1.07
TCDD TEQs (a)	0.23	0.2049	0.0059	0.2200	nr	0.56	0.6	14.00	0.05
Naphthalene	0.00	0.0003	0.0000	0.0179	0.0003	0.017	0.019	33.8	0.0006
Phenanthrene	0.01	0.0008	0.0001	0.0109	0.0003	0.018	0.021	33.8	0.00062
DDTS	0.00	0.0003	0.0000	0.0001	0.0000	0.00198	0.00225	0.0028	0.80
PCBs	0.04	0.0081	0.0004	0.0063	0.0001	0.04	0.05	0.180	0.28
								Hazard Index	5.78

a — 2,3,7,8-TCDD TEQs in ng/kg, ww

b — Hazard Quotient is adjusted to account for 100% of diet, assuming equal contamination of the 25% unsampled.

nr: analyte not reported in this media

Table 7-14b. Ingestion rates and doses of CoCs, by media,
with Hazard Quotient calculations for the black-crowned night heron.

Housatonic Boat Club Wetlands

Contaminant of Concern	Dietary Intake, (mg/day)					Total Assimilated (mg/day)	Total Assimilated (mg/kg Bw/day)	RTV (mg/kg Bw/day)	Hazard Quotient
	Fish	Crab	Insects	Sediment	Water				
Arsenic	nc	0.0956	nc	0.0450	0.0009	0.1	0.1	5.14	0.03
Cadmium	nc	0.0025	nc	0.0067	0.0001	0.01	0.01	1.45	0.006
Chromium (+3)	nc	0.1095	nc	1.4000	0.0032	1.3	1.5	1.00	1.46
Copper	nc	4.9181	nc	4.8200	0.0075	6.3	7.2	28.13	0.26
Lead	nc	2.5130	nc	1.2200	0.0020	3.2	3.6	2.05	1.75
Mercury	nc	0.0008	nc	0.0040	0.0002	0.004	0.005	0.0320	0.15
Nickel	nc	0.1233	nc	0.1850	0.0001	0.26	0.3	77.4	0.0038
Silver	nc	nr	nc	0.0060	0.0001	0.005	0.006	12.50	0.0005
Zinc	nc	1.2997	nc	1.6620	0.0008	2.5	2.9	11.3	0.25
TCDD TEQs (a)	nc	0.7517	nc	0.1350	nr	0.75	0.9	14.00	0.06
Naphthalene	nc	0.0001	nc	0.0083	0.0003	0.007	0.008	33.8	0.0002
Phenanthrene	nc	0.0001	nc	0.0026	0.0003	0.003	0.003	33.8	0.00009
DDTS	nc	0.0000	nc	0.0001	0.0000	0.00006	0.00007	0.0028	0.03
PCBs	nc	0.0747	nc	0.0027	0.0001	0.07	0.07	0.180	0.41
								Hazard Index	4.40

a — 2,3,7,8-TCDD TEQs in ng/kg, ww

b — Hazard Quotient is adjusted to account for 100% of diet, assuming equal contamination of the 25% unsampled.

nr: analyte not reported in this media

Table 7-14c. Ingestion rates and doses of CoCs, by media,
with Hazard Quotient calculations for the black-crowned night heron.

Milford Point Reference Area

Contaminant of Concern	Dietary Intake, (mg/day)					Total Assimilated (mg/day)	Total Assimilated (mg/kg Bw/day)	RTV (mg/kg Bw/day)	Hazard Quotient
	Fish	Crab	Insects	Sediment	Water				
Arsenic	0.08	0.0814	0.0007	0.0370	0.0003	0.2	0.2	5.14	0.04
Cadmium	0.00	0.0042	0.0020	0.0055	0.0000	0.01	0.01	1.45	0.010
Chromium (+3)	0.39	0.1785	0.0046	1.2130	0.0009	1.5	1.7	1.00	1.72
Copper	1.20	2.5207	0.0790	4.3470	0.0010	5.3	6.0	28.13	0.21
Lead	0.11	0.1754	0.0192	0.4210	0.0002	0.6	0.7	2.05	0.34
Mercury	0.00	0.0011	0.0000	0.0038	0.0003	0.007	0.008	0.0320	0.24
Nickel	0.08	0.1315	0.0021	0.1440	0.0001	0.30	0.3	77.4	0.0044
Silver	0.01	nr	nr	0.0040	0.0001	0.011	0.012	12.50	0.0010
Zinc	7.57	1.1242	0.2316	1.7560	r	9.1	10.3	11.3	0.91
TCDD TEQs (a)	0.12	0.1096	0.0037	0.0450	nr	0.24	0.3	14.00	0.02
Naphthalene	0.00	0.0002	0.0000	0.0019	0.0003	0.002	0.003	33.8	0.0001
Phenanthrene	0.00	0.0001	0.0001	0.0019	0.0003	0.002	0.003	33.8	0.00008
DDTS	0.01	0.0002	0.0000	0.0000	0.0000	0.00471	0.00534	0.0028	1.91
PCBs	0.25	0.0029	0.0004	0.0014	0.0001	0.22	0.25	0.180	1.39
								Hazard Index	6.76

a — 2,3,7,8-TCDD TEQs in ng/kg, ww

b — Hazard Quotient is adjusted to account for 100% of diet, assuming equal contamination of 25% unsampled.

nr: analyte not reported in this media

r: concentration data rejected

Table 7-15. Ingestion rates and doses of CoCs, by media, with Hazard Quotient calculations for the red-winged Black Bird.

Ferry Creek

Contaminant of Concern	Dietary Intake, (mg/day)		Total Assimilated[a] (mg/day)	Total Assimilated[b] (mg/kg Bw/day)	RTV (mg/kg Bw/day)	Hazard Quotient
	Insects	Water				
Arsenic	0.01	0.0000	0.0	0.1	5.14	0.02
Cadmium	0.02	0.0037	0.02	0.36	1.45	0.248
Chromium (+3)	0.02	0.0002	0.0	0.3	1.00	0.34
Copper	0.64	0.0021	0.4	7.0	28.13	0.25
Lead	0.05	0.0208	0.1	1.0	2.05	0.50
Mercury	0.00	0.0024	0.002	0.037	0.0320	1.15
Nickel	0.02	0.0001	0.02	0.3	77.4	0.0038
Silver	nr	0.0020	0.002	0.029	12.50	0.0023
Zinc	1.78	0.0003	1.5	25.3	11.3	2.24
TCDD TEQs[c]	0.05	nr	0.04	0.7	14.00	0.05
Naphthalene	0.00	0.0009	0.001	0.015	33.8	0.0005
Phenanthrene	0.00	0.0009	0.001	0.021	33.8	0.00061
DDTS	0.00	0.0000	0.00023	0.00391	0.0028	1.40
PCBs	0.00	0.0000	0.00	0.05	0.180	0.29
					Hazard Index	6.48

a — Adjusted for bioavailability factor.

b — Adjusted for 90% home range factor.

c – 2,3,7,8-TCDD TEQs in ng/kg, ww

nr: analyte not reported in this media

r: concentration data rejected

Table 7-15, (con't). Ingestion rates and doses of CoCs, by media, with Hazard Quotient calculations for the red-winged Black Bird.

Milford Point Reference Area

Contaminant of Concern	Dietary Intake, (mg/day)		Total Assimilated[a] (mg/day)	Total Assimilated[b] (mg/kg Bw/day)	RTV (mg/kg Bw/day)	Hazard Quotient
	Insects	Water				
Arsenic	0.0058	0	0.0049	0.08	5.14	0.02
Cadmium	0.017	0.0008256	0.0156	0.26	1.45	0.18
Chromium (+3)	0.040	0.00012	0.0339	0.57	1.00	0.57
Copper	0.68	0.0027348	0.45	7.43	28.13	0.26
Lead	0.17	0.0030788	0.1434	2.39	2.05	1.17
Mercury	0.00035	0.0005676	0.0008	0.01	0.0320	0.40
Nickel	0.018	0.001032	0.0161	0.27	77.4	0.0035
Silver	nr	0.0003096	0.0003	0.00	12.50	0.00035
Zinc	2.00	r	1.7018	28.36	11.3	2.51
TCDD TEQs[c]	0.032	nr	0.0270	0.45	14.00	0.03
Naphthalene	0.00023	0.00086	0.0009	0.015	33.8	0.00046
Phenanthrene	0.00108	0.00086	0.0016	0.03	33.8	0.0008
DDTS	0.00028	0	0.0002	0.004	0.0028	1.40
PCBs	0.0032	0	0.0027	0.05	0.180	0.25
					Hazard Index	6.79

a — Adjusted for bioavailability factor.

b — Adjusted for 90% home range factor.

c — 2,3,7,8-TCDD TEQs in ng/kg, ww

nr: analyte not reported in this media

r: concentration data rejected

Table 3-3.1. Ingestion rates and doses of CoCs by media, with Hazard Quotient calculations for the black-crowned night heron.

A. Upper Ferry Creek (MF03)

Contaminant of Concern	Dietary Intake, (mg/day)					Total Assimilated		RTV	Hazard Quotient
	Fish	Crab	Insects	Sediment	Water	(mg/day)	(mg/kg Bw/day)	(mg/kg Bw/day)	
Arsenic	nr	nr	nr	nr	nr	nr	nr	5.14	nr
Cadmium	nr	nr	nr	nr	nr	nr	nr	1.45	nr
Chromium (+3)	nr	nr	nr	nr	nr	nr	nr	1.00	nr
Copper	nr	nr	nr	nr	nr	nr	nr	28.13	nr
Lead	nr	nr	nr	nr	nr	nr	nr	2.05	nr
Mercury	nr	nr	nr	nr	nr	nr	nr	0.0320	nr
Nickel	nr	nr	nr	nr	nr	nr	nr	77.4	nr
Silver	nr	nr	nr	nr	nr	nr	nr	12.50	nr
Zinc	nr	nr	nr	nr	nr	nr	nr	11.3	nr
TCDD TEQs (a)	0.0002	nr	nr	nr	nr	0.0002	0.0002	14.00	0.00001
Naphthalene	nr	nr	nr	nr	nr	nr	nr	33.8	nr
Phenanthrene	nr	nr	nr	nr	nr	nr	nr	33.8	nr
DDTs	nr	nr	nr	nr	nr	nr	nr	0.0028	nr
PCBs	0.09	nr	nr	nr	nr	0.08	0.09	0.180	0.47
								Hazard Index	0.47

a — 2,3,7,8-TCDD TEQs in ng/kg, ww

b — Hazard Quotient is adjusted to account for 100% of diet, assuming equal contamination of the 25% unsampled.

nr: analyte not reported in this media

Table 3-3.1 (con't). Ingestion rates and doses of CoCs by media, with Hazard Quotient calculations for the black-crowned night hero

B. Middle Ferry Creek (A3SD10)

Contaminant of Concern	Dietary Intake, (mg/day)					Total Assimilated		RTV	Hazard Quotient
	Fish	Crab	Insects	Sediment	Water	(mg/day)	(mg/kg Bw/day)	(mg/kg Bw/day)	
Arsenic	nr	nr	nr	0.24	nr	0.2	0.2	5.14	0.04
Cadmium	nr	nr	nr	0.08	nr	0.07	0.08	1.45	0.055
Chromium (+3)	nr	nr	nr	4.63	nr	3.9	4.5	1.00	4.46
Copper	nr	nr	nr	25.5	nr	21.7	24.5	28.13	0.87
Lead	nr	nr	nr	32.9	nr	28.0	31.7	2.05	15.45
Mercury	nr	nr	nr	0.004	nr	0.004	0.004	0.0320	0.13
Nickel	nr	nr	nr	3.17	nr	2.69	3.1	77.4	0.0394
Silver	nr	nr	nr	0.02	nr	0.017	0.019	12.50	0.0015
Zinc	nr	nr	nr	13.4	nr	11.4	12.9	11.3	1.14
TCDD TEQs (a)	0.0003	nr	nr	0.01	nr	0.0055	0.0063	14.00	0.00045
Naphthalene	nr	nr	nr	0.01	nr	0.009	0.010	33.8	0.0003
Phenanthrene	nr	nr	nr	0.01	nr	0.007	0.008	33.8	0.00022
DDTs	nr	nr	nr	nr	nr	nr	nr	0.0028	nr
PCBs	0.10	nr	nr	0.29	nr	0.33	0.38	0.180	2.09
								Hazard Index	24.28

a — 2,3,7,8-TCDD TEQs in ng/kg, ww

b — Hazard Quotient is adjusted to account for 100% of diet, assuming equal contamination of the 25% unsampled.

nr: analyte not reported in this media

Table 3-3.1 (con't). Ingestion rates and doses of CoCs by media, with Hazard Quotient calculations for the black-crowned night heron

C. Lower Ferry Creek (SD26)

Contaminant of Concern	Dietary Intake, (mg/day)					Total Assimilated		RTV	Hazard Quotient
	Fish	Crab	Insects	Sediment	Water	(mg/day)	(mg/kg Bw/day)	(mg/kg Bw/day)	
Arsenic	nr	nr	nr	nr	nr	nr	nr	5.14	nr
Cadmium	nr	nr	nr	nr	nr	nr	nr	1.45	nr
Chromium (+3)	nr	nr	nr	nr	nr	nr	nr	1.00	nr
Copper	nr	nr	nr	nr	nr	nr	nr	28.13	nr
Lead	nr	nr	nr	nr	nr	nr	nr	2.05	nr
Mercury	nr	nr	nr	nr	nr	nr	nr	0.0320	nr
Nickel	nr	nr	nr	nr	nr	nr	nr	77.4	nr
Silver	nr	nr	nr	nr	nr	nr	nr	12.50	nr
Zinc	nr	nr	nr	nr	nr	nr	nr	11.3	nr
TCDD TEQs (a)	0.0002	nr	nr	nr	nr	0.0002	0.0002	14.00	0.00001
Naphthalene	nr	nr	nr	nr	nr	nr	nr	33.8	nr
Phenanthrene	nr	nr	nr	nr	nr	nr	nr	[illegible]8	nr
DDTs	nr	nr	nr	nr	nr	nr	nr	0.0028	nr
PCBs	0.09	nr	nr	nr	nr	0.08	0.09	0.180	0.47
								Hazard Index	0.47

a — 2,3,7,8-TCDD TEQs in ng/kg, ww

b — Hazard Quotient is adjusted to account for 100% of diet, assuming equal contamination of the 25% unsampled.

nr: analyte not reported in this media

Table 3-3.1 (con't). Ingestion rates and doses of CoCs by media, with Hazard Quotient calculations for the black-crowned night heron

D. Great Meadows Reference Area (GM08)

Contaminant of Concern	Dietary Intake, (mg/day)					Total Assimilated		RTV	Hazard Quotient
	Fish	Crab	Insects	Sediment	Water	(mg/day)	(mg/kg Bw/day)	(mg/kg Bw/day)	
Arsenic	nr	nr	nr	0.18	nr	0.2	0.2	5.14	0.03
Cadmium	nr	nr	nr	0.02	nr	0.01	0.01	1.45	0.010
Chromium (+3)	nr	nr	nr	2.31	nr	2.0	2.2	1.00	2.22
Copper	nr	nr	nr	6.6	nr	5.6	6.4	28.13	0.23
Lead	nr	nr	nr	1.6	nr	1.3	1.5	2.05	0.74
Mercury	nr	nr	nr	0.012	nr	0.010	0.012	0.0320	0.36
Nickel	nr	nr	nr	0.37	nr	0.32	0.4	77.4	0.0047
Silver	nr	nr	nr	0.03	nr	0.026	0.029	12.50	0.0023
Zinc	nr	nr	nr	2.9	nr	2.5	2.8	11.3	0.25
TCDD TEQs (a)	0.0003	nr	nr	0.0001	nr	0.0004	0.0004	14.00	0.00003
Naphthalene	nr	nr	nr	0.01	nr	0.006	0.006	33.8	0.0002
Phenanthrene	nr	nr	nr	0.001	nr	0.001	0.001	[illegible]8	0.00003
DDTs	nr	nr	nr	nr	nr	nr	nr	0.0028	nr
PCBs	0.10	nr	nr	0.003	nr	0.08	0.10	0.180	0.53
								Hazard Index	4.39

a — 2,3,7,8-TCDD TEQs in ng/kg, ww

b — Hazard Quotient is adjusted to account for 100% of diet, assuming equal contamination of the 25% unsampled.

nr: analyte not reported in this media

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Draft

Evaluation of Raymark Superfund Data for PRG Development

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11 February 1998

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1.0. INTRODUCTION

The purpose of this study is to evaluate historical and recently collected chemistry and toxicity data for development of Preliminary Remediation Goals for Raymark-related Contaminants of Concern (CoCs). PRG's are risk-based chemical criteria which are intended to be protective of site biota. PRGs require site-specific evaluation because either applicable criteria are not available for important CoCs, or available literature values are not considered to be adequately protective under site-specific conditions.

Three primary components of PRG development include assessment of CoC-related risks due to chemical exposure via aquatic, terrestrial and human health exposure pathways. This report focuses primarily on the development of PRGs for protection of aquatic life; a final section involves the assessment of potential impacts of bioaccumulative CoCs (i.e., dioxins, PCBs) on avian predators consuming fish from the Raymark study area. Human health risks are beyond the scope of the present investigation.

PRG development for protection of aquatic life involves the inspection of existing or new data containing paired chemistry-toxicity measurements. These data form the basis of "exposure-response" relationships, where increasing adverse effects are observed with increasing chemical concentration. The CoC-specific PRG is developed by selecting the contaminant concentration that results in an unacceptable adverse effect. Multiple CoCs are evaluated in a similar manner and inter-compared to determine which PRG is most protective, considering both the concentration and the associated uncertainty about the estimate. In instances like Raymark where a mixed waste contains multiple CoCs, the selection process would typically yield a few PRGs which may be applied to the site depending on station-specific CoC concentrations. These PRGs are assumed to be protective for effects due to the mixed waste as a whole, i.e., other CoCs at lower effects-based concentrations would be remediated in association with the clean-up based on the selected PRGs.

The method for application of the PRG to the site for delineation of areas concern requires consideration of CoC spatial distributions; this step, however, is beyond the scope of the present objectives.

2.0. MATERIALS AND METHODS

Collection (Section 2.1), chemical evaluation (Section 2.2) and toxicity testing (Section 2.3) methodologies for sediments are presented in the sections below.

2.1. Field Collection Methodology

Sample locations for the present evaluation included 19 locations in the Raymark study area and one reference location (Figure 2.1-1). Sediments were collected over a three day period in August 1997. The majority of sediments were sampled by hand with scoops from just above

the tide line within two hours of low tide. Four subtidal sampling locations in the lower Ferry Creek area were sampled from a small boat equipped with a davit and modified 0.1 m^2 Young grab sampler. Both intertidal and subtidal samples were collected to approximately 6" depth until 5 gal. of wet sediment were obtained. Care was taken to prevent loss of fines as well as to minimize the entrainment of excess water into the sample. Clean techniques were employed during all sampling procedures and chain of custody procedures were followed. After each day of collection, samples were placed on ice and transported by van to the SAIC Environmental Testing Laboratory (ETC) in Narragansett, RI and stored at 4°C until needed.

Fish samples were also taken at three Raymark stations (SD26, A3SD10, MF03) and at the reference location (GM08; Figure 2.1-1). Minnow traps were baited with bread and placed in the subtidal zone at low tide and connected via line to a shoreline stake. Minnow traps were checked twice daily at low tide until sufficient numbers of the target species (*Fundulus heteroclitus*) were obtained for chemical analysis. Fish were transferred from the traps to clean glass jars after each collection and placed on ice for transport to the ETC. At the laboratory, arriving samples were subsequently composited (within station) with previous samples and frozen at -20°C until needed.

2.2. Chemical Analytical Methods.

Chemical analyses included evaluations of bulk sediment (Section 2.2.1), sediment porewater (Section 2.2.2) and fish tissue (Section 2.2.3), and supporting non-CoC parameters (DOC, TOC, lipids; Section 2.2.4).

2.2.1. Bulk Sediment Analyses

PCBs. Given the need to collect both PCB congener/homolog and the more traditional Aroclor data, two different procedures were employed. The PCB congener and homolog analyses were conducted using a modification of EPA Method 680. Briefly, it is a GC/MS procedure that employs a low resolution mass spectrometer in the selected ion monitoring (SIM) mode. For the purposes of this project, that method has been modified so as to obtain results for the various PCB congener and homologs in Table 1. As modified, the PCBs are separated by the GC and quantitated using an isotope dilution procedure that requires that stable isotopically-labeled analogs representing at least one PCB congener in each homolog be added to the sample prior to the start of the extraction procedure.

The Aroclor data were generated using a modification of the U.S. EPA Contract Laboratory Program (CLP) Statement of Work (SOW) for organic analyses, OLM03.0. The CLP SOW employs a GC/EC instrument to separate and quantify the Aroclor mixtures. Analyses of Aroclor mixtures are highly dependant on the interpretive skill of the analyst, although the CLP method requires that 3 to 5 characteristic peaks for each Aroclor be used to quantitate the sample results. One significant modification of the CLP was the addition of Aroclors 1262 and 1268 to the series of standards prior to sample analysis. The results of those analyses were used by the

analyst for the purposes of pattern recognition, and to choose the characteristic peaks that are used for quantitation.

SVOCs. SVOC analyses were performed following the protocols specified in the CLP SOW OLM03.0 (with revisions). The percent moisture of the sediment samples was determined prior to sample extraction or analysis and sample volumes adjusted to achieve desired quantitation limits (dry basis) for all sediment samples regardless of the high moisture content of the samples. Samples were maintained at 4 degrees C (± 2 degrees C) consistent with the CLP instruction procedures for sample storage.

Metals. The metal analysis were performed by the U.S. EPA CLP SOW for Inorganic Analysis, Multi-media, Multi-concentration ILM03.0 (and revisions) without modification. The percent moisture of the sediment samples was determined prior to sample extraction or analysis and sample volumes adjusted to achieve desired quantitation limits (dry basis) for all sediment samples regardless of the high moisture content of the samples.

2.2.2. Sediment Porewater Analyses

Fifteen of the twenty samples were selected for detailed chemical and toxicological analysis. The primary criterion for selection for further analysis was the observation of significant toxicity (<80% survival) using the 10-day solid phase test with the amphipod *Ampelisca abdita* (discussed below). This test is an accepted indicator of the potential for toxic risk and the test protocol method is an EPA standard (USEPA, 1994).

Organics Sample Preparation - All reagents used were of pesticide grade or better. Fifty mL (50 mL) of sample was spiked with internal standards, PCBs 103 and 198, for use in quantifying the chlorinated pesticides, DDT and metabolites, and PCB congeners. For PAHs, 5 alpha androstane was used as the internal standard.

Porewater samples were collected using the syringe extraction technique of Winger and Lassier (1991). Samples were sonicated for 1 minute with 10 mL of extraction solvent in a 40 mL centrifuge tube and centrifuged for 5 minutes. The solvent was removed and reserved, and the procedure repeated for a total of three times yielding 30 mL of extract per sample. Each extract was combined in a bottle with 70 mL of 2% sodium sulfate in deionized water washed with solvent. The solvent - sodium sulfate solution was triple extracted using 10 mL each time of extracting solvent compatible with the analytes of interest. The resulting extract was dried over sodium sulfate to remove any water in the extract, and reduced in volume to approximately 5 mL by nitrogen evaporation. A 300 mm X 10 mm i.d. liquid chromatography column with reservoir, stopcock, and coarse fritted disk was packed with 3.5 g of florisil and topped with 1.5 g of sodium sulfate for organochlorine and PCB compounds. For PAH compounds the column was packed with 10 g of silica gel in methylene chloride and topped with 2 g of sodium sulfate. For organochlorine and PCB compounds the column was washed with 20 mL hexane. For PAHs the column was washed with 20 mL of pentane. When the hexane (or pentane) had nearly reached

the top of the sodium sulfate. the 5 mL of sample extract was quantitatively transferred to the column. For chlorine and PCB compounds, the column was eluted with 40 mL of 10% ethyl ether in hexane. For PAHs the column was eluted first with 20 mL of petroleum ether, followed by 40 mL of 10% methylene chloride in petroleum ether. The samples were collected from each column and reduced in volume to 1 mL by nitrogen evaporation in concentrator tubes. The extract was transferred to a GC autosampler vial, sealed, and stored until analysis.

Inorganics Sample Preparation- Samples were prepared using microwave digestion. Three to five g of sample was treated with 5 mL concentrated nitric acid, 2 mL of concentrated hydrochloric acid, and 3 mL of deionized water. The digest was allowed to cool, and volumetrically diluted to a final volume of 100 mL.

Instrumental Analyses - MDLs (method detection limits) were established for each analyte before analyses were conducted. MDLs was obtained for the procedures outlined in 40 CFR part 136, and in Standard Methods for the Examination of Water and Wastewater.. Water MDLs for organic and inorganic compounds were reported as µg/L.

All analyses for organics were performed using Hewlett-Packard model 5890 series II or 6890 series capillary GCs equipped with dual autosamplers. Splitless injection was used. Fused silica capillary columns used for each channel of the GC for organochlorine and PCB analyses were 60 m, 0.25 mm i.d., with a 0.25 micron film thickness DB-5 or equivalent. PAH analyses columns were 30 m, 0.25 mm i.d., with a 0.25 micron film thickness DB-5 or equivalent. Ultra high purity Helium was the carrier gas in each GC. For each sample batch of ten, a three point calibration curve was established.

For organochlorine/PCB analyses, the GC was equipped with dual electron capture detectors (ECDs), injection ports, and autosampler. Temperature programming was used to chromatograph the samples. The injector temperature was 280 degrees C and the detector temperature was 310 degrees C. For PAH analyses, the GC was equipped with a flame ionization detector (FID), set at the correct hydrogen and air flow rates. The injector temperature was 300 degrees C and the detector temperature was 325 degrees C. As with Organochlorine/PCB analyses, temperature programming was used to chromatograph the samples.

For metal analyses, a Varian SpectrAA 20 flame atomic absorption spectrophotometer and a Varian SpectrAA 400 Zeeman graphite furnace atomic absorption spectrophotometer were used to determine the concentration of trace metals. Each unit was equipped with data stations and autosamplers. For all metal analyses, a three point calibration curve plus blank was established.

2.2.3. Fish Tissue Analyses

As part of this project, data on polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in fish tissue samples was required. The analytical method employed was EPA Method 1613B. In addition to the 17 2,3,7,8-substituted PCDDs/PCDFs addressed in that method, data also were obtained the "total" concentrations in each level of chlorination, e.g., total TCDD. Method 1613B includes procedures for acid/base back extraction, gel permeation chromatography (GPC), silica gel, alumina, and activated carbon column cleanups, and an anthropogenic isolation column for the removal of lipids. For the purposes of this project, the analysis methods of the fish tissue samples were selected to meet the MDLs for the solid samples, e.g., 1 ng/kg for TCDD, up to 10 ng/kg for OCDD. Any sample in which 2,3,7,8-TCDF was observed above the MDL was confirmed by analysis on a second column, as described in Section 16.5 of Method 1613B.

2.2.4. DOC/TOC/Lipid Analyses

Finally, in order to assess the bioavailability of these contaminants, measurements are needed of the dissolved organic carbon (DOC) in the pore water samples (EPA Method 415.1), the total organic carbon (TOC) of the sediments (EPA Method 415.1), and the lipid content of the tissue samples (Bligh and Dyer, 1959).

2.3. Toxicity Testing

Toxicity analyses included evaluations of bulk sediment (Section 2.2.1), sediment porewater (Section 2.2.2) and chemically fractionated porewater (Section 2.2.3).

2.3.1. Bulk Sediment Tests

For whole sediment tests, the 5 gal samples were homogenized using stainless steel paddles. Bulk sediments were evaluated in the 10-day solid-phase amphipod test using the marine amphipod, *Ampelisca abdita* according to EPA procedures (USEPA, 1994). The test was conducted for 10 days using 1 L glass jars containing 175 mL of homogenized sediment and 800 mL of overlying seawater collected from lower Narragansett Bay, RI. Exposure was static at 20°C with a continuous lighting. Test chambers were aerated to maintain acceptable oxygen levels. Twenty subadult test organisms per chamber, which were not fed during the test, were used. Water quality parameters were monitored: pore water ammonia was measured at the beginning of the test; overlying water ammonia, pH, salinity, and dissolved oxygen was measured at the beginning and the end of the test; and temperature was recorded daily in one chamber and continuously in the water bath. Survival, measured as the number live retrieved at the end of the test compared to the number added, was determined. Survival was compared to a "clean" laboratory performance control sediment.

2.3.2. Sediment Porewater Tests

For pore water tests, samples were collected according to methods described by Winger and Lasier (1991). Briefly, sediments were homogenized as described above and interstitial water was collected using a vacuum-operated pore water extractor constructed from fused glass airstones attached to a 60 cc syringe. The airstone was inserted into the sediment and a vacuum was created by retracting and bracing the syringe plunger.

Pore waters were used to determine survival effects to *Ampelisca abdita* in 48-hour and 96-hour water-only tests and development effects to the marine bivalve, *Mulinia lateralis*, in 48-hour water-only tests. A concentration series was used so that a threshold concentration (i.e., LC50 for the amphipod test and EC50 for the bivalve test) could be determined.

Water-only tests using *Ampelisca abdita* were performed according to EPA procedures (USEPA, 1996). The test was conducted for 48 or 96 hours using 30 mL plastic cups and 15 mL of sample. A concentration series (e.g., 0, 10, 50 and 100% or 0, 6.25, 12.5, 25, 50, and 100% sample) with natural seawater collected from lower Narragansett Bay as diluent. Exposure was static at 20°C with a 16 hour light and 8 hour dark cycle. Five subadult test organisms per chamber, which were not fed during the test, were used. Ammonia, salinity, and pH were measured in the samples. Survival, measured as the number live retrieved at the end of the test compared to the number added, was determined. The LC50, the concentration at which survival was reduced by 50%, was calculated using ToxCalc®.

Tests using *Mulinia lateralis* were also performed according to EPA procedures (USEPA, 1996). The test was conducted for 48 hours using 30 mL plastic cups and 10 mL of sample. A concentration series (e.g., 0, 10, 50 and 100% or 0, 6.25, 12.5, 25, 50, and 100% sample) with natural seawater collected from lower Narragansett Bay as diluent. Exposure was static at 20°C with a 16 hour light and 8 hour dark cycle. Three hundred embryos were added to each chamber. Embryos were not fed during the test. Ammonia, salinity, and pH were measured in the samples. Development, measured as the number of normal embryos out of 100 embryos counted, was determined. The EC50, the concentration at which normal development was reduced by 50%, was calculated using ToxCalc®.

2.3.3. Fractionated Porewater Tests

Pore waters were amended or fractionated using marine toxicity identification evaluation (TIE) methodologies (USEPA, 1996). Three amending procedures were performed using the pore water to identify potential contaminants of toxicological concern: the C18 solid-phase extraction column (SPEC) was used to remove nonionic organic compounds, EDTA (ethylenediaminetetraacetic acid) was used to bind divalent cationic metals (e.g., copper, nickel, lead, zinc, cadmium, and mercury), and the macroalgae *Ulva lactuca* or sea lettuce was used to remove ammonia (ULVA). Amended samples were evaluated using the aqueous phase amphipod and bivalve tests. Threshold concentrations for fractionated samples were compared

to non-fractionated sample responses.

SPEC. Methanol (25 mL) and DI (25 mL) were used to prepare columns for sample passage. A continuous flow rate 7-10 mL/min was used. Natural seawater passed through the column served as a laboratory performance control and was used to prepare dilutions of amended pore waters.

EDTA. EDTA (25 g EDTA in 1 L of DI)) was added to each sample so that the final concentration was 60 mg or 0.22 mmol EDTA per L of sample. The sample was mixed thoroughly. Test organisms were added after three hours. EDTA was added to natural seawater to serve as a laboratory performance control and for dilutions of amended pore waters.

ULVA. *Ulva lactuca* was collected from Narragansett Bay just prior to use. Debris and white or yellow tips were discarded. Sea lettuce samples were rinsed in clean seawater, patted dry and added to salinity adjusted samples so that each 60 mL of sample contained 5 g of lettuce. Sample salinity was adjusted using brine (i.e., 2X GP2 in natural seawater) prepared according to EPA (1994). Samples with *Ulva* were aerated gently under laboratory lights for five hours. Lettuce was removed and animals were added. Ammonia was measured before and after treatment with *Ulva*. Natural seawater was treated with sea lettuce to serve as a laboratory performance control and for dilutions of amended pore waters.

3.0. RESULTS AND DISCUSSION

3.1. Toxicity Testing

3.1.1. Bulk Sediment Toxicity

Results of bulk sediment tests with amphipods are summarized in Table 3.1-1. Of the 20 sediment samples tested, 5 samples exhibited survival > 85% and were excluded from further analyses. Among the remaining 15 samples, four samples were non-toxic (exhibiting survival $\geq$ 80%; "-"), four samples were slightly toxic (survival between 50-80%; "+"), five samples were moderately toxic (survival between 20-50%; "++"), and two samples were highly toxic (survival < 20%; " +++"). Some the samples had relatively high total and un-ionized ammonia concentrations, exceeding the NOEC values for this species (30 and 0.4 mg/L, respectively). However, the affected samples (SD07, SD08, and SD28) were no more than slightly toxic, such that ammonia did not appear to be a significant confounding factor in interpretation of results of these bulk sediment tests. Hence, the observed range of survival was expected to provide an adequate range of toxicity and associated chemical concentration in sediment porewaters for TIE evaluations, discussed below.

3.1.2. *Porewater/TIE Toxicity*

Porewater toxicity results for *Ampelisca* (survival) and *Mulinia* (larval development), discussed below, are expressed as the concentration of porewater required to affect 20% of the test population (i.e., EC20). A 20% effect level was selected as being more environmentally conservative than a 50% reduction (e.g., LC50 or EC50) as organisms can be exposed to 100% porewater in the field, and because the approach provided a more dynamic range in the data set (multiple values with LC50 values ">100%" can have lower and different values as LC20 estimates). This calculation is an interpolated value based on exposure-response results of the 48hr porewater exposures for the control (0% porewater) and each of five dilution series (6.25%, 12.5%, 25%, 50% and 100%) as summarized in Appendix Tables B-1 to B-4.

Ampelisca Toxicity. Results of sediment porewater tests with *Ampelisca* are reported in Table 3.1-2. The data include tests with whole porewater (PW), as well as chemically-treated porewater to selectively remove organics (C18) and metals (EDTA).

An initial comparison of porewater EC20 results with that of bulk sediment tests relative to overall sample toxicity (High, Intermediate, Low, Non-toxic) indicate that two of 15 samples (A3SD10 and HB3A) were significantly lower in toxicity (two categories lower toxicity in porewater than sediment), while two additional samples (SD08 and SD37) were significantly higher in toxicity (two categories higher toxicity in porewater than sediment). Hence, the majority of samples exhibited comparable toxicity between sediment and porewater exposures.

The LC20 results for *Ampelisca* in whole porewater ranged from a low of 25.0% (SD18) to a high of 100% (e.g., non-toxic, SD28). Stations ranked with highest toxicity ("++"; SD01, SD08, SD18 and SD37) for the porewater treatment also tended to have the highest total and/or unionized ammonia concentrations in porewater bioassays which were about 2-fold greater than the NOEC concentration. An increase in ammonia concentration is believed to have occurred during holding between the time of bulk sediment and porewater extraction.

Inspection of the EDTA and C18 fractionation results for amphipods (Table 3.1-2) indicates results for 9 of 15 stations did not change from the corresponding porewater result (i.e., LC20 within 10%), while five samples (A3SD10, GM08, SD01, SD08 and SD37) had a similar reduction in toxicity (i.e., +10% change in LC20 for both EDTA and C18 treatment vs. PW treatment). Among the remaining samples, C18 treatment increased toxicity in one sample (HB3A), but decreased toxicity in another (SD07). Thus on the basis of toxicity results alone, the TIE fractionation tests with *Ampelisca* were inconclusive with respect to the relative role of metals vs. organics in CoC-related impacts. However, these results will be explored further when toxicity results are compared to matching porewater chemical analyses (Section 3.4).

As discussed in the methods section, a porewater collection technique using syringe extraction was preferred as it presented the best approach for minimizing handling artifacts with regard to the bioavailability of CoCs in the sample. Because of the concern over potential non-

CoC toxicity related to ammonia/sulfides, an aeration experiment with *Ampelisca* was conducted to assess the effect of sample oxidation on toxicity. The non-aerated exposure portion of the test employed the same test methods as the previous porewater test, while split samples were taken and bubbled with air for 60 minutes prior to testing.

Although direct sulfide measurements on the preparations were not performed, those samples with increased high ammonia are also expected to contain sulfides because ammonia production is a precursor to sulfide generation in sediments. Hence, porewaters which are highest in ammonia should be most susceptible to an aeration effect resulting in increased toxicity if the oxidation of sulfides are allowing metals in solution to become bioavailable, or alternatively, decrease in toxicity if ammonia concentration is the primary constituent caused adverse impact.

Results presented in Table 3.1-3 show that five of 15 samples (SD07, SD13, SD14, SD24 and SD37) increased in toxicity, while only one sample (SD28) decreased in toxicity as a result of aeration. Another four samples (HB3A, SD01, SD18 and SD23) remained completely toxic, thus leaving open the possibility that aeration could have increased CoC bioavailability, although it cannot be proven without performing testing on diluted samples. Still, those samples which increased in toxicity also had relatively high ammonia whereas the three non-toxic samples (A3SD10, CSD1, GM08) which were low in ammonia were unaffected by aeration.

These results are consistent with the hypothesis that aeration increases toxicity because sulfide oxidation allows previously bound metals in solution to become bioavailable. Hence, the anoxic nature of sediments (whether naturally or anthropogenically induced) under existing conditions in the Raymark study area may presently afford a substantial degree of protection to indigenous biota to metals toxicity.

Mulinia toxicity. Results of larval development tests with *Mulinia* exposed to whole porewater and TIE fractions (EDTA, C18) are presented in Table 3.1-4. The *Mulinia* results generally indicated higher levels of effects than did *Ampelisca*; the EC20 values for whole porewater range from 0.4 - 55.7%, indicating that all porewater samples resulted in reduction in larval development success, and over half (9 of 15) samples had high (EC20 < 10%) toxicity. This enhanced toxicity is at least partially attributed to the fact that the *Mulinia* test is a sub-lethal, larval stage test, whereas the *Ampelisca* endpoint is survival of the adult stage. As observed for *Ampelisca*, measured ammonia concentrations were above the LC50 values for both total (13 mg/L) and unionized (0.2 mg/L) forms, such that a portion of toxicity may not be directly related to CoC concentration.

The EDTA and C18 treatment of split samples and retesting with *Mulinia* resulted in a comparable range of EC20 values. There was a general trend for the EDTA treatment to reduce sample toxicity as compared to that for whole porewater; three samples (A3SD10, GM08 and SD07) exhibited a > 10% reduction in toxicity, while only one sample (SD23) appeared to have a comparable increase in toxicity. As discussed for the amphipod results, reduced toxicity is

expected if the EDTA treatment was effective in sequestering metals from solution. A similar result was observed for the C18 treatment; three samples exhibited reduced toxicity (SD18, SD2: and SD24). Because EDTA and C18 treatments affected different samples and the general trend was to reduced toxicity, it would appear that the TIE results hold promise for segregating metals vs. organics toxicity. The significance of these results will be further evaluated from examinatior of exposure-response relationships from which CoC-specific contributions may be discerned.

Ulva Treatments. Ulva treatments of porewater were conducted to address residual toxicity associated with ammonia in the sample. For *Ampelisca*, test durations were extended to 96 hr so as to increase the threshold of detection toxicity related to CoC in the sample. Results presented in Table 3.1-5 show that only 5 of 15 samples (HB3A, SD01, SD14, SD18, and SD21) remained toxic after *Ulva* treatment. (Note the reduction in ammonia concentration relative to the whole porewater tests). The lack of toxicity does not contraindicate the possibility of CoC related toxicity in whole porewater samples since *Ulva* may be capable of uptaking the CoCs and hence reducing chemical bioavailability (see Section 3.2, below). Rather the data do suggest that those samples which remain toxic after *Ulva* treatment are likely to have CoCs at effect-causing concentrations without masking due to ammonia effects; these data will be utilized further in PRG development discussed in Section 4.

Ulva treatments of porewater were also conducted using *Mulinia* as had been done for Ampelisca (split samples). Results presented in Table 3.1-5 show that the majority of samples exhibited comparable toxicity between non-*Ulva* and *Ulva*-treated porewater, while three of 15 samples (GM08, SD13 and SD28) were more toxic after *Ulva* treatment. The continued toxicity of the samples despite ammonia removal indicates that CoCs are likely to be present at toxic concentrations. The cause of increased toxicity is uncertain, although laboratory studies have demonstrated that Ulva may release exudates which are toxic to *Mulinia* (Johnson and Welsh, 1985).

3.2. Chemical Analytical Results

Results for chemical analysis of bulk sediment, porewater and tissue samples respectively are reported in Sections 3.2.1, 3.2.2 and 3.2.3., below.

3.2.1. Bulk Sediment Chemistry

Data presented in Table 3.2-1 provides a brief description of sediment concentrations relative to NOAA ER-M benchmarks (expressed as Hazard Quotients, HQ) for Raymark sampling locations selected for TIE analyses. Among the metals, copper, nickel, lead and zinc were found at concentrations which exceeded the respective ER-M benchmarks. Complete results are presented in Appendix Table A-2-1.1. The results were qualitatively scaled so as to facilitate the data presentation as follows: concentrations < ER-M were flagged as "-", values 1> ER-M <2 were flagged as "+", values 2 < ER-M <10 were flagged as "++", and values > 10X ER-M were flagged as "+++". Lead was the most pervasive CoC in exceedence of the ER-M

(12 of 15 stations), followed by copper (10 of 15 stations), nickel and zinc (8 of 15 stations). Chromium and mercury also exceeded the ER-M on two occasions. With regard to the magnitude of contamination, one station in particular (HB3A) stands apart with HQs for copper and lead >> 100, while a second station (A3SD10) has a copper and lead HQs of 9.5 and 15.1, respectively. The remainder of stations have relatively lower CoC concentrations, with Hazard Index (sum of metal-specific HQs) values in the range of 4-18.

As for PAHs, the Hazard Index for four stations (SD07, SD13, SD14 and SD23) had dibenz(a,h)anthracene, fluorene, and phenanthrene concentrations exceeding the ER-M by more than two-fold, and corresponding HI > 20. PCB concentrations also appeared substantially elevated at a number of stations.

Because only six of the quantified congeners are in common with the 18 congeners used by NOAA for the Total PCB determination, there existed uncertainty in the sum of congeners estimate of Total PCBs for comparison against the NOAA ER-M benchmark. To address this issue, six samples were selected for additional congener quantitation to obtain the full NS&T congener complement. Regression analysis of Total PCBs by congener method (sum of NS&T congeners x 2) against sum of PCB homologs revealed a linear relationship Figure 3.2-2). This excellent agreement permitted prediction of Total PCBs for comparison against the ER-M benchmark, discussed below.

The results of PCB ERM-HQs show patterns similar results as for the metals; Station HB3A stands apart with the PCB HQ = 1762, while two additional stations (A3SD10 and SD01) have HQs >> 100. Except for Station GM08 and SD37 (HQ < 1.5), the remaining stations have HQs in the range of 5 - 50. Finally, the pesticide p,p'-DDE was quantified for three stations (HB3A, SD07 and SD21) and was not found to be present in high concentrations (HQ << 1).

SEM:AVS measurements on bulk sediments were performed to assess potential divalent metal bioavailability and associated potential toxicity to benthic infauna. Numerical values for SEM constituents (Cu, Cd, Ni, Pb and Zn) are presented in Appendix Table A-5; results are presented graphically in Figure 3.2-1. Among the 15 sampling locations, three stations (A3SD10, HB3A, SD18) were noted to have sum SEM concentrations (μMol/g dry wt) which exceeded AVS concentration (noted by asterisk), hence indicating potential toxicity. These stations, among others, were founded to be toxic to amphipods as discussed above (Table 3.1-1). The relationship between SEM concentrations and concentrations of metals in porewater will be discussed in Section 3.4.5.

3.2.2. Porewater Chemistry

Data presented in Table 3.2-2 provides a similar description of porewater concentrations and Hazard Quotients as discussed for sediments, above. Complete results are presented in Appendix Table A-2-2.1. In this analysis, however, porewater concentrations are compared to Water Quality Screening Values (WQSV, units = μg/L) with CoC-specific benchmarks being

obtained from amphipod LC50 values where available, or otherwise taken from EPA Water Quality Chronic Values. Among the metals, copper clearly emerges as the principal CoC of concern, with HQs > 1 at all but one station (SD18). Arsenic exceed the WQSV at four stations (CSD1, SD07, SD08, and SD13), while zinc exhibited HQs > 1 at two locations (A3SD10, GM08). With regard to the magnitude of contamination, Station HB3A stands apart an HQ for copper ~30, while a second station (A3SD10) has a copper and lead HQs of 9.5 and 15.1, respectively. The remainder of stations have relatively lower CoC concentrations, with Hazard Index (sum of metal-specific HQs) values in the range of 2-10. Station SD18 was the only location with an HI < 1.

Porewater PAH concentrations were less than the Method Detection Limit of 1 µg/L at almost all of the stations. The sole exception was found for benzo(a,h)anthracene at Station SD13 (HQ =40). These results would generally suggest that PAHs are an unlikely contributor to porewater toxicity, although uncertainty exists for those PAHs with WQSV values < 1 µg/L. PCB concentrations were substantially elevated at six stations, including CSD1, SD07, SD08, SD13, SD23 and SD28), while concentrations at the remaining stations were below detection (1 µg/L). As was done for sediments, the sum of congeners x 2 was calculated for comparison against the EPA benchmark, although in this case, the 18 congeners used by NOAA for the Total PCB determination were employed. Three stations (SD07, SD08 and SD24) had Total PCB HQs of ~50, two stations (CSD1, SD23) were ~ 30, and one station (SD13) was ~13. The fact that these data do not appear to correlate well with the respective sediment based concentrations is attributed mainly to differences in congeners quantified for the respective analyses. A more detailed analysis is presented in Section 4, below.

3.2.3. TIE Chemistry

Based on results of porewater metals analyses, samples were selected for chemical analyses following further TIE manipulation including C18, EDTA, and ULVA treatment. Sample selection was prioritized for those samples where analytes were present at concentrations exceeding detection and with porewater HQs > 1.

Samples treated with EDTA for metals reduction were analyzed for PCBs; results are reported in Appendix Table A-1-2.2 for the six PCB samples which had detectable concentrations in porewater. Results show that detectable PCB concentrations were found in only three of the six samples, and total concentrations were reduced by a factor of 10 or more. This unexpected result could not be explained by preferential removal of certain PCB congeners, as the congener mixtures did not change in any predictable manner. One consistent relationship that was observed was the correlation between the retention of PCBs in the sample and the presence of higher DOC (Appendix Table A-1-5), and silt/clay content (Appendix Table A-1-4).

Samples treated with C18 for organics reduction were analyzed for seven metals; concentrations and associated Hazard Quotients results are reported in Appendix Tables A-1-2.3 and A-2-2.3, respectively. Copper was the most prevalent CoC with concentrations exceeding

the WQSV; HQs > 1 were observed for eight of 15 stations. The highest observed HQ was found for Station HB3A (HQ = 4.10), while remaining exceedances had HQs < 2. Arsenic also was found to exceed the WQSV at four locations (CSD1, SD07, SD08, and SD28) with HQs 1-2. Finally, zinc concentrations exceeded the WQSV at two locations, Station A3SD10 (HQ = 7.0) and Station GM08 (HQ= 1.49). Additional samples were also analyzed for PCB concentrations to confirm the C18 removal efficiency (Appendix Table A-2-4.); concentrations were almost entirely less than the MDL (1 µg/L) in almost all samples.

A final set of samples were subjected to *Ulva* treatment for purposes of ammonia reduction. Samples were analyzed prior to and after *Ulva* treatment, and included both PCB and selected metals. The effectiveness for removal of ammonia by *Ulva* was previously demonstrated by data presented in Table 3.1-4. Results are reported in Appendix Table A-1-2.4. With the exception of Station SD01, PCB concentrations were below detection in all samples. As for metals, results were generally within two-fold concentration difference for respective *Ulva* and non-*Ulva* treated samples and no apparent trend due to treatment was observed. Hence it was concluded that the *Ulva* treatment should provide adequate data for the assessment of metals related toxicity without interference by PCB or ammonia.

3.3. Trophic Transfer Assessment

Not completed.

3.4. PRG Development

The objective of PRG development is to derive class- and/or analyte-specific criteria for metals and organics contaminants in sediments related to the Raymark site. For the PRG to be site-specific, it necessary to assess both the inherent toxicity of the chemical in the sediment mixture as well as the contribution the CoC makes to the overall toxicity of the sample. Because there is a lack of knowledge of how site-specific conditions may modify chemical bioavailability and the nature of non-linear interactions among CoCs which may modify toxicity, it is not possible to complete this evaluation using solely literature-based values. Rather re-testing of sediments is required in a manner which permits developing quantitative relationships between the toxicity of the sample and the concentration of the site-related CoCs.

Toxicity Identification Evaluation (TIE) involves chemical manipulation of field samples to separate CoC classes, such that CoC-specific exposure-response relationships can be developed. The work performed includes testing of both whole sediment and whole porewater collected from stations of suspected toxicity as well as the partitioning of CoCs in porewater into metals and organics fractions for separate characterization.

As noted above, *Ampelisca* was chosen for these tests because of its amenability to this type of short-term exposure. The bivalve, *Mulinia lateralis*, was chosen for the TIE testing because of its ease of handling and culture in the laboratory, its wide range of salinity tolerance,

and the ability to produce embryos for testing on-demand. This last characteristic is the most compelling reason in the selection of this species as a surrogate for the oyster, *Crassostrea virginica*. It also is more appropriate to utilize a ubiquitous eastern bivalve as a surrogate for *C. virginica* than to use the west coast species *C. gigas* which was previously used in the Raymark Ecological Risk Assessment (NOAA, 1996).

As discussed above, porewater fractionation (TIE) procedures included two primary manipulation methods: EDTA chelation to bind metals and effectively remove them from the mixture; and C18 column extraction to remove organic compounds. The interpretation of the TIE data with regards to identifying the chemicals responsible for causing observed toxicity was accomplished according to the following approach:

- Assess the magnitude of porewater CoC exceedence of benchmarks in relation to sample toxicity was used to derive thresholds below which adverse effects would be unexpected, called the Threshold Effect Quotient (TEQ; Section 3.4.1);
- Separately determine TEQs for CoCs in TIE fractions (Section 3.4.2);
- Intercompare whole porewater and TIE TEQs for the species tested to identify primary CoCs for PRG development, and select range of appropriate porewater concentrations that do not pose a toxic risk (Section 3.4.3);
- Translate TEQ values to whole sediment concentrations to determine Aquatic Preliminary Remediation Goals and assess selected PRGs against sediment based results and results of the Ecological Risk Assessment to verify PRG effectiveness aquatic for risk reduction (Section 3.4.4).

A brief description of each step in the interpretive framework is provided below.

3.4.1. Porewater Toxic Units (TUs)

As discussed above, two test species were utilized as surrogates for aquatic Receptors of Concern at the Raymark site. The bivalve *Mulinia lateralis* was employed as a surrogate for the American oyster and the amphipod *Ampelisca abdita* as a surrogate for appropriately sensitive benthic organisms. *Ampelisca* was also the organism used in the whole sediment tests and thus provides a common basis for relating sediment to porewater toxicity, particularly because species-specific data are available as to the concentration of individual chemicals in undiluted porewater sample ($[PW_{CoC}]$) expected to cause 50% reduction in survival (LC50) in single toxicant laboratory bioassays. These data are used to quantify the overall toxicity of samples from a chemical perspective as the number of "toxic units" for the CoC ($IWTU_{CoC}$) as follows:

$$1)\ IWTU_{CoC} = [PW_{CoC}]/LC50_{CoC};$$

The above procedure is repeated for each of the CoCs of interest in the sample and IWTUs summed to obtain the ΣIWTU (Sum Interstitial Water Toxic Units) for the sample. Because species-specific data for *Mulinia* are not available, LC50 values for *Ampelisca* were assumed to be comparable.

Results of IWTU and ΣIWTU calculations for porewater exposure to *Ampelisca* and *Mulinia* is reported separately for metals and organics in Table 3.4-1. For the metals, only arsenic, cadmium, copper and zinc were found to occur at concentrations in porewater that were at least 10% of the LC50 value (i.e., IWTU > 0.1); other analytes were excluded from analysis since these CoCs were unlikely to substantially contribute to the toxicity of the sample. The Table includes ranked toxicity results paired with corresponding IWTUs, segregated by degree of toxicity (High, Intermediate, Low, Non-toxic). A Threshold Effect Quotient (TEQ) is also calculated for each CoC and used as a point of reference to identify CoCs and associated concentrations which might be contributing to increased sample toxicity. The TEQ is taken as the maximum IWTU value of the least toxic sample group, or where this IWTU value is less than unity, a TEQ = 1 was adopted. It is expected that site-specific conditions in sediments of the Raymark study area might result in TEQ values greater than one as a given CoC could be less toxic in the field sample than under the water only, single toxiciant test conditions in which the LC50 values were derived. Similarly, it was assumed that field conditions would not increase the toxicity of a given CoC to levels greater than that afforded in the laboratory tests, such that TEQ values < 1 would be considered spurious (and leading to a minimum TEQ = 1).

Results of exposure-response analyses for *Ampelisca* in whole porewater are presented in Table 3.4-1A. Among the metals, 46% of the samples were above the ΣIWTU TEQ (4.5) with copper and arsenic providing the majority contribution to the total. Copper and arsenic also had the highest frequency of TEQ exceedence; 31% of samples exceeding the TEQ were toxic. In contrast, none of the toxic samples were associated with elevated PAH or PCB concentration. Toxic units calculated for total ammonia did indicate that elevated toxicity in some samples (23%), might be unrelated to CoC exposure; however in only one of the six samples (Station SD01) did metal-related toxicity also coincide with elevated ammonia (TU > 1.0). Hence it is concluded that copper and arsenic may be the primary CoCs contributing to porewater toxicity to amphipods.

A similar exposure-response analysis for *Mulinia* is presented in Table 3.4-1B. In this instance, all samples exhibited some toxicity; although results for Station SD28 (EC20 = 55.7) were clearly less toxic than the remainder of samples. Using the SD28 result as the basis of comparison, 57% of the samples were above the metal ΣIWTU TEQ (4.1) with copper and arsenic providing the majority (amount and frequency) contribution to the total. As observed for Ampelisca, none of the toxic samples were associated with elevated PAH or PCB concentration. Again, toxic units calculated for total ammonia did indicate that elevated toxicity in a number of samples (57%), but still the predicted contribution from metals was more than twice that for ammonia, such that it may reasonably concluded that metals are the primary contributors to

sample toxicity. Results of TIE analyses presented below will more directly address the relativ contribution of ammonia to overall sample toxicity.

3.4.2. Relative Toxicity of Metals and Organics

The EDTA and C18 column manipulations (USEPA, 1996) were used to segregate the relative contributions to total toxicity from either metals or organic compounds, respectively. Presented in Table 3.4-2 are toxicity and IWTU data obtained after passing of the whole porewater sample through a carbon-activated (C18) column to remove organic contaminants. Only the ammonia data were not directly measured after C18/EDTA treatments.

Metals. The exposure-response analysis for *Ampelisca* in C18-treated porewater is presented in Table 3.4-2A. As a whole, the samples were generally less toxic in comparison to the whole porewater treatment results (perhaps due to ammonia removal). Copper exceeded the TEQ (1.46) in 20% of the cases, whereas arsenic, cadmium and zinc IWTUs were not associated with toxic samples. It is also noted that the total IWTU value was not predictive of toxicity in any of the samples, which suggests that CoCs other than copper are not substantially contributin to sample toxicity.

The corresponding exposure-response analysis for *Mulinia* in C18-treated porewater is presented in Table 3.4-2B. The range of observed toxicity was also somewhat less than that observed for the whole porewater treatment results (again, perhaps due to ammonia removal), bu still, copper is identified as the primary CoC exceeding the TEQ (1.37), with arsenic and zinc being secondary but significant contributors to overall sample toxicity as noted from the total IWTU values.

Organics. The exposure-response analysis for *Ampelisca* in EDTA-treated porewater is presented in Table 3.4-3A. As a whole, the samples exhibited similar toxicity in comparison to the whole porewater treatment results. Two treated samples were found to have PCB concentrations above the TEQ, however, the degree of observed toxicity was comparable or less than that of other samples where PCB concentrations were below detection. Hence it is concluded that PCBs and PAHs are not likely to be primary contributors of toxicity in the samples and that non-CoC constituents such as ammonia are the cause of reduced toxicity.

The exposure-response analysis for *Mulinia* in EDTA-treated porewater is presented in Table 3.4-3B. In general, the samples exhibited slightly lower toxicity in comparison to the whole porewater treatment results. The distribution of toxicity followed the *Ampelisca* EDTA results in that two treated samples were found to have PCB concentrations above the TEQ, but again, the degree of observed toxicity was comparable to or even less than that of other samples where PCB concentrations were below detection. Hence it is again concluded that PCBs and PAHs are not likely to be primary contributors of toxicity in the samples and that non-CoC constituents such as ammonia are the cause of reduced toxicity in these samples.

Ammonia. A final TIE analysis was conducted to more directly assess the contribution of ammonia to overall sample toxicity. Results reported in Table 3.4-4 for *Ampelisca* and *Mulinia* include a comparison of toxicity responses between sample porewater treated with *Ulva* to remove ammonia and the untreated response as previously reported in Table 3.4-1.

Four samples selected for chemical analyses show comparable chemical concentrations before and after *Ulva* treatment and highly effective ammonia removal in the *Ulva* treatment as expected (Table 3.4-4). For *Ampelisca* (Table 3.4-4A), copper was again identified as the primary CoC contributing to toxicity in the Ulva treatment, with zinc contributing a minor fraction to the sample Total IWTU at Station HB3A. In addition, the estimated TEQ values were highly comparable between Ulva and non-Ulva exposures. Hence, it is concluded that the presence of ammonia in the samples did not significantly alter the TEQs derived from the data.

As with *Ampelisca*, copper was again identified as the primary CoC contributing to toxicity to *Mulinia* in the Ulva treatment (Table 3.4-4B), and zinc also contributed slightly to Total IWTU at one location (Station HB3A). More importantly, ammonia removal did not result in reduced toxicity, and because the estimated TEQ values were comparable between Ulva and non-Ulva exposures, it is concluded that the presence of ammonia in the samples did not significantly alter the TEQs derived from the data.

3.4.3. TEQ Intercomparisons

Table 3.4-5 provides a summary of TEQ values and frequency of exceedence as derived from *Ampelisca* and *Mulinia* exposures to whole porewater, C18 and EDTA treatments. For metals, TEQ values over the entire data set range from 1.0-2.6, with the copper TEQ exceeded most frequently (26.1%) among the 15 sampled locations. For some CoCs, the frequency of exceedence was so low as to merit rejection as PRGs; PCBs, cadmium, and zinc were observed above the TEQ value less than 10% of the time. The arsenic TEQ appeared potentially more relevant to *Mulinia* than to *Ampelisca* as deduced from frequency of exceedence, although the species and test-specific estimates were within two-fold magnitude of each other. In addition, arsenic was not one of the CoCs identified as being elevated in sediments (discussed in Section 3.2); half of the samples were less than the ER-L concentration, and the highest value was less than 3 fold higher than the ER-L (Station A3SD10, ERL-HQ = 2.91). Hence, the data would suggest that copper is the primary constituent in porewater causing toxicity, with a threshold for effects in the range of 1.4 (*Mulinia*, C18 treatment) to 2.7 (*Mulinia* and *Ampelisca;* whole porewater treatment) times the LC50 value (20.5 µg/L). The section below presents calculations used to derive the PRG (sediment equivalent concentration) comparable to this copper TEQ value.

3.4.4. Calculating Sediment-based PRG Concentrations

During the present investigation, results of bulk sediment testing with *Ampelisca* have identified eleven toxic sediments with three of the sediments having SEM-AVS concentrations

exceeding unity, hence the likelihood for metals-related effects. The fact that more sediments did not exhibit SEM-related toxicity is most certainly due to high acid volatile sulfides in the samples which generally ranged from 6-12 μMol/g dry weight. Because of sample volume requirements and concern over the vertical representation of surface samples, the sampling depth was extended to approximately 12-15 cm below the sediment water interface. Field observations noted a very shallow apparent Redox Potential Depth (RPD), such that collected sediments were in many cases anoxic and hence likely to retain sulfides. Hence it is likely that measured toxicity may have under-represented the true potential toxicity of sediments in the oxygenated sediment-water interface zone where AVS would be oxidized and less available to bind divalent metals. In addition, seasonality and resuspension events may cause AVS concentrations to fluctuate (Peterson *et al.*, 1996).

As discussed in Section 3.2, the predominant metals found in the SEM fraction of sediment were zinc and lead at concentrations 2-6 μMol/g dry weight. In contrast, nickel generally contributes < 1 μMol/g dry wt, while cadmium and copper combined contribute less than 0.1 μMol/g dry wt. Hence in presence of reduced AVS concentration, zinc, lead and to a lesser extent, nickel, may combine to produce total SEM concentrations which exceed AVS, such that PRG concentrations corresponding to the SEM conditions would be desirable.

Relationships presented in Figure 3.4-1 demonstrate that SEM concentrations of lead, zinc and nickel (as discerned from the slope of the curves) are approximately 0.2%, 0.5% and 0.1% of the respective analyte concentrations in bulk sediment. These relationships can be used to estimate SEM concentrations from bulk sediment data, as follows:

$$2)\quad \text{SEM}\ (\mu\text{Mol/g dry}) = 0.002[\text{Pb}] + 0.005[\text{Zn}] + 0.001[\text{Ni}],$$

where [Pb], [Zn] and [Ni] are the bulk sediment concentrations of lead, nickel and zinc, respectively. For example, a sediment containing 1000 ppm each of the three metals would have and equivalent SEM concentration of 8 μMol/g dry weight. Oxidized sediments would not be expected to have AVS > 1 μMol/g, such that the hypothetical sediment SEM-AVS would be > seven, representing a free SEM concentration expected to be toxic. Thus sediment based PRGs should be selected for these three metals, and could be derived from a statistical probability distribution of the entire site data set collected as part of the FS investigation. It is noted that results of the Ecological Risk Assessment as analyzed in SAIC, (1997) show reduced diversity and number of species at SEM concentrations > 10 μMol/g dry wt.

Porewater and TIE testing has directed the focus on copper as the primary CoC of concern, with the upper range of no to low toxic effects determined for two species/life stages (*Ampelisca* survival, *Mulinia* larval development success). Relationships between copper concentrations in porewater and corresponding concentrations measured in bulk sediment are depicted in Figure 3.4-2. The strongest relationship is apparent between porewater concentration and the TOC normalized sediment concentration ($y = 0.23X+29.1$; $r^2 = 0.99$). This result is in agreement with findings of Mahony *et al.* (1996) which showed that porewater concentrations of

divalent metals, particularly copper, may be strongly influenced by the TOC content of sediment. Interpolating the copper TEQ range of 1.4-2.7 (28.7 - 55 µg/L), the corresponding sediment concentration can be estimated in the range of 4.2 - 111.6 µg Cu/mg TOC. Subsequently, the median site-wide concentration of TOC in sediment (7.8% = 78 mg TOC/g sediment; Appendix A-1-4.2) can be applied to approximate the sediment-based PRG concentration (329 µg/g to 8700 µg/g dry wt). Perusal of copper concentrations in sediment (Appendix A-1-1) finds that 66% (10/15) of the sediments exceed the more conservative PRG estimate. As discussed above for SEM data, a more detailed analysis of the entire copper data set collected as part of the FS investigation could provide a statistical probability distribution to determine the potentially affected area.

Finally, data on sediment dioxin concentrations were collected primarily to support assessment of potential food chain transfer to fish and aquatic birds (discussed in Section 3.4.3). Apart from the potential risks to fish and wildlife, an analysis was conducted to further evaluate the potential exposure response relationship between amphipod survival and dioxin concentration deduced from the ERA (as reported in SAIC 1997). The results of the analysis is presented in Figure 3.4-3, where all amphipod samples exhibited intermediate toxicity (< 50% survival) at Total Toxicity Equivalency concentrations > 150 ng/g dry weight. Perusal of the dioxin data reported in Appendix A-1-6) finds that 33% (5/15) of the sediments exceed this threshold for amphipod toxicity. As discussed above for the SEM/ data, a more detailed analysis of the entire dioxin data set should be performed to determine the potentially affected area and need for adopting a sediment-based PRG for dioxin.

4.0 SUMMARY

Toxicity Testing

- Bulk sediment tests with *Ampelisca* identified 15 stations (out of 20) with mean survival less than 85%. These locations were selected for subsequent porewater and TIE evaluations.

- Good agreement was found between *Ampelisca* bulk sediment survival and porewater EC20 endpoints with respect to sampling location and qualitative extent of toxicity;

- On the basis of toxicity results alone, the EDTA and C18 TIE fractionation tests with *Ampelisca* were inconclusive with respect to the relative role of metals vs. organics in CoC-related impacts.

- Porewater aeration of high ammonia samples increased sample toxicity; it is postulated that this effect may be caused by release of metals during acid volatile sulfide oxidation.

- Unlike *Ampelisca* exposures, EDTA and C18 TIE fractionation tests with *Mulinia* caused differential reductions in sample toxicity, hence providing valuable data for segregating metals vs. organics effects.

Chemical Analytical Results

- In sediments, copper, nickel, lead and zinc were found at concentrations which often exceeded the respective ER-M benchmarks. In contrast, arsenic, chromium and mercury only occasionally exceeded ER-L benchmarks. Four of 15 sampling locations had PAH analyte concentrations exceeding ER-M concentrations. Thirteen of 15 sampling locations had Total PCB concentrations exceeding ER-M values; however uncertainty exist due to the composition of congeners used in the calculation.

- For sediment porewaters, concentrations were normalized to Water Quality Screening Values (*Ampelisca* LC50, EPA WQC- Saltwater Chronic Values) to derive Interstitial Water Toxic Units (IWTUs). Among the metals, copper clearly emerges as the principal CoC of concern, with IWTUs > 1 at all but one station, followed by arsenic (four stations) and zinc (two stations). PCBs were substantially elevated at six stations, but non-detect in the remaining samples. PAHs were almost entirely less than 1 µg/L in all samples.

- In samples treated with EDTA for metals reduction, detectable PCB concentrations were found in only three of the six samples, and total concentrations were reduced by a factor of 10 or more.

- In samples treated with C18 for organics reduction, copper was the most prevalent CoC with concentrations exceeding the WQSV for eight of 15 stations; PCBs were non-detect in all samples.

- Samples were subjected to *Ulva* treatment for purposes of ammonia reduction. Samples chemically analyzed after *Ulva* treatment had substantial PCB loss; concentrations were below detection in all samples while metals were generally within two-fold of non-*Ulva* treated samples.

PRG Development

- The magnitude and frequency of porewater CoC exceedence of benchmarks in relation to sample toxicity was used to derive CoC-specific values below which adverse effects would be unexpected, called the Threshold Effect Quotient (TEQ).

- Results of porewater exposure-response analyses for *Ampelisca* and *Mulinia* suggest that copper and arsenic were the primary CoCs with IWTUs above the TEQ, whereas none of the toxic samples had elevated PAH or PCB IWTUs.

- The C18 treatment of porewater were used to separately address the relative contributions to total toxicity from individual metals. For *Ampelisca*, only copper was associated with toxic samples above the TEQ (1.46; 20% frequency). For Mulinia assays, copper was the main CoC exceeding the TEQ (1.37; 25% frequency), while exceedences of the arsenic TEQ (1.47; 16.7% frequency) and zinc TEQ (1.0, 16.7% frequency) were also noted.

- The EDTA treatment of porewater were used to separately address the relative contributions to total toxicity from individual organic compounds. For *Ampelisca*, only PCBs were occasionally associated with toxic samples above the TEQ (1.00; 16.7% frequency). Similarly for *Mulinia*, only PCBs were occasionally associated with toxic samples above the TEQ (1.00; 15.4% frequency). In both cases, however, the degree of observed toxicity was comparable or less than that of other samples where PCB concentrations were below detection, such that it was concluded that PCBs are not likely to be primary contributors of toxicity.

- A final TIE analysis using Ulva-treated porewater to more the contribution of ammonia to overall sample toxicity. Chemical analyses show comparable metals concentrations before and after *Ulva* treatment and complete ammonia removal in the *Ulva* treatment. Copper was again identified as the primary CoC contributing to toxicity in the *Ulva* treatment for both *Ampelisca* and *Mulinia* tests, and estimated TEQ values were comparable between *Ulva* and non-*Ulva* exposures. Hence, it is concluded that the presence of ammonia in the samples did not significantly alter the TEQs derived from the data.

- In considering TEQ values and frequency of exceedence as derived from *Ampelisca* and *Mulinia* exposures to whole porewater, C18 and EDTA treatments; the data suggest that copper is the primary constituent in porewater causing toxicity, with a threshold for effects in the range of 1.4 to 2.7 times the LC50 value (20.5 µg/L).

- With regard to the bioavailability of sediment metals, the potential for reduced AVS concentration in surface sediments raises concern that presently bound SEM metals could become toxic. A modelwas developed to predict SEM concentration from bulk sediment concentrations such that PRGs for lead and zinc can be evaluated.

- A TOC-dependent model relating copper concentrations in porewater and corresponding bulk sediment concentrations was developed for calculation of the copper PRG. From the model, a the sediment-based PRG concentration of 329 µg/g to 8700 µg/g dry wt. Approximately 66% (10/15) of the sediments collected from the present investigation exceed the more conservative PRG estimate.

- Finally, data on sediment dioxin concentrations were evaluated to assess potential risks to aquatic birdsfrom consumption of sediment and fish. An exposure response relationship between amphipod survival and dioxin concentration was observed where Total Toxicity Equivalency (Teq) concentrations > 150 ng/g dry weight were associated with intermediate to high toxicity. About 33% (5/15) of the sediments exceed this threshold for amphipod toxicity.